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PATENT ABSTRACTS OF JAPAN

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(54) MANUFACTURING METHOD FOR THERMOPLASTIC RESIN PARTICLE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide such a method for manufacturing thermoplastic resin particles as simplifying a separating process of resin particles and a drying process of resin particles.

SOLUTION: The manufacturing method for thermoplastic resin particles comprises the steps of obtaining a thermoplastic resin particle dispersion by dispersing in a melt state the resin containing a thermoplastic resin (B) into a supercritical fluid obtained by heating under pressure a compound (A), which gasifies at 25 °C under 101.3 KPa, to a condition under more than the critical pressure of and at more than the critical temperature of the compound (A), then of cooling and pressure-reducing the system, and consequently of removing the compound (A) from the thermoplastic resin particle dispersion by vaporizing the compound (A) in the thermoplastic resin particle dispersion.

JAPANESE

[JP,2004-323727,A]

Drawing selection **Drawing 1**

CLAIMS DETAILED DESCRIPTION TECHNICAL
FIELD PRIOR ART EFFECT OF THE INVENTION
TECHNICAL PROBLEM MEANS EXAMPLE
DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

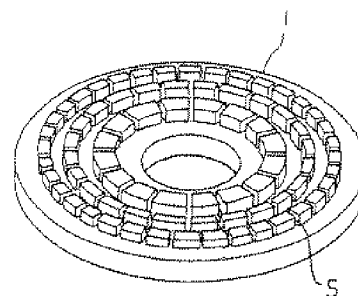
[Field of the Invention]

This invention relates to the manufacturing method of the simplified thermoplastic resin particle which does not perform the partition process of a resin particle, and the drying process of a resin particle but with which thermoplastic resin particles can also manufacture **.

[0002]

[Description of the Prior Art]

The coloring resin melting object which carries out heating fusion of the kneaded material of the synthetic resin for toners and paints which have an ionic group as a manufacturing method of resin particles, such as a toner, for example, Maintaining the temperature of a mixture to the temperature more than the softening temperature of the synthetic resin for toners using the mixture which mixed the aqueous medium heated to the temperature more than the softening temperature of the synthetic resin for toners including the substance which neutralizes an ionic group.



[Translation done.]

Micro-disperse of the coloring resin melting object is carried out into an aqueous medium, by cooling quickly promptly after that, the water dispersion of a coloring resin particulate is manufactured and there is a manufacturing method of the toner for electrostatic charge image development which performs separation of a coloring resin particulate and desiccation from these dispersion liquid (for example, refer to patent documents 1.). However, said manufacturing method is a time-consuming manufacturing method which consists of a process of melting of a synthetic resin, the distribution to an aqueous medium, separation of the resin particle from dispersion liquid, and desiccation of a resin particle, and the manufacturing method which carried out simple [of the process] more is called for.

[0003]

[Patent documents 1]

JP,9-311502,A (the two - 8th page)

[0004]

[Problem(s) to be Solved by the Invention]

The technical problem of this invention is providing the manufacturing method of the simplified thermoplastic resin particle which does not perform the partition process of a resin particle, and the drying process process of a resin particle but with which thermoplastic resin particles can also manufacture **.

[0005]

[Means for Solving the Problem]

This invention persons found out following (1) and knowledge of (2), as a result of inquiring wholeheartedly.

(1) Supercritical fluid produced by 25 ** and 101.3KPa by carrying out application-of-pressure heating of the compound (A) used as a gas more than the critical pressure of a compound (A) and more than critical temperature is used, distributing a resin melting object which contains thermoplastics (B) in this supercritical fluid by a molten state -- a thermoplastics grain -- a henchman -- a powder object can be manufactured.

(2) said thermoplastics grain -- a henchman -- performing cooling and decompression of a system, after manufacturing a powder object -- a thermoplastics grain -- a henchman -- powder -- like said patent documents 1, since a compound (A) in the living body evaporates and it is easily removed from a dispersing element, [and] A drying process is not performed, but a thermoplastic resin particle is obtained and ** can also simplify a manufacturing process.

This invention is completed based on the above-mentioned knowledge.

[0006]

Namely, in supercritical fluid which is produced by 25 **

and 101.3KPa by carrying out application-of-pressure heating of the compound (A) used as a gas more than the critical pressure of a compound (A), and more than critical temperature as for this invention, After distributing a resin melting object containing thermoplastics (B) by a molten state and obtaining a thermoplastic resin particle dispersing element, by performing cooling and decompression of a system, a thermoplastics grain -- a henchman -- powder -- making a compound (A) in the living body evaporate -- a thermoplastics grain -- a henchman -- a manufacturing method of a thermoplastic resin particle removing a compound (A) from a powder object is provided.

[0007]

[A mode of implementation of an invention]

Hereafter, this invention is explained in detail.

As 25 ** used by this invention, and a compound (A) which serves as a gas by 101.3KPa, oxygen, nitrogen, hydrogen, air, carbon dioxide, ammonia, methane, ethylene, ethane, propane, butane, etc. are mentioned, for example.

Compound of a compound (A) whose critical temperature is 5-100 ** and whose critical pressure is 2 - 10MPa is preferred, and critical temperature is 10-50 **, A compound whose critical pressure is 4 - 8MPa is more preferred, and carbon dioxide (critical temperature is 31.1 ** and the critical pressure is 7.38MPa) is especially the most preferred.

[0008]

As thermoplastics (B) used by this invention, For example, styrene acrylic resin; styrene butadiene series copolymer; polyester resin, such as a styrene acrylic ester system copolymer and a styrene methacrylic-acid-ester system copolymer; hybrid resin of styrene acrylic resin and polyester resin, etc. are mentioned. As for weight average molecular weight of thermoplastics (B), 2,000-200,000 are preferred, 3,000-80,000 are more preferred, and 5,000- especially 20,000 are preferred. As softening temperature by a ring and ball method of thermoplastics (B), For example, in a thermoplastic resin particle obtained with a manufacturing method of this invention, a toner and when using as color toner preferably, fixability and heat-resistant cohesiveness are good, Since coiling round or an offset phenomenon of paper to a fixing roll of a copy machine do not happen easily, 70-200 ** is preferred, 70-130 ** is more preferred, and especially 90-120 ** is preferred. When using a thermoplastic resin particle obtained with a manufacturing method of this invention as a toner for full color as a glass transition point of thermoplastics (B), for example, since fixability and heat-resistant cohesiveness are good, 55-75 ** is preferred and 60-70 ** is more preferred.

[0009]

Since the dispersibility of paints is good and the color enhancement of paints also has it when distributing paints and considering it as coloring resin, thermoplastics (B) used by this invention has preferred polyester resin. [good]

[0010]

Said polyester resin mixes polybasic acid of three or more organic functions, and polyhydric alcohol of three or more organic functions with dicarboxylic acid, or its anhydride and diol if needed, and is obtained by performing dehydration condensation, for example. Various catalysts can be added in order to promote a dehydrating condensation reaction at this time.

[0011]

As said catalyst, a zinc oxide, tin, dibutyl tin oxide, dibutyltin dilaurate, Para toluenesulfonic acid, tetrabutyl titanate, etc. are mentioned, for example.

[0012]

As said dicarboxylic acid, aliphatic dicarboxylic acid and aromatic dicarboxylic acid, such as line aliphatic dicarboxylic acid and cyclic aliphatic dicarboxylic acid, etc. are mentioned, for example. As aliphatic dicarboxylic acid, a maleic anhydride, fumaric acid, succinic acid, an alkenyl succinic anhydride, adipic acid, cyclohexanedicarboxylic acid, etc. are mentioned, for example. As aromatic dicarboxylic acid, terephthalic acid, isophthalic acid, phthalic anhydride, naphthalene dicarboxylic acid, etc. are mentioned, for example. Aromatic dicarboxylic acid of dicarboxylic acid is preferred, and its terephthalic acid is especially more preferred.

[0013]

As said diol, aliphatic series diol and aromatic diol, such as line aliphatic series diol and cyclic aliphatic series diol, etc. are mentioned, for example. As said line aliphatic series diol, for example Ethylene glycol, a diethylene glycol, Triethylene glycol, propylene glycol, dipropylene glycol, Tripropylene glycol, butanediol, pentanediol, hexanediol, A polyethylene glycol, a polypropylene glycol, ethylene oxide propylene oxide random copolymer diol, Ethylene oxide propylene oxide block copolymer diol, ethylene oxide tetrahydro franc copolymer diol, polycaprolactone diol, etc. are mentioned.

[0014]

As cyclic aliphatic series diol, 1,4-cyclohexane dimethanol, 1,4-cyclohexane dimethanol, 1,4-cyclohexanediol, etc. are mentioned, for example.

[0015]

As aromatic diol, for example Polyoxyethylene (2.0)-2,2-bis (4-hydroxyphenyl)propane, Polyoxypropylene (2.0)-2,2-bis

(4-hydroxyphenyl)propane, Polyoxypropylene (2.2)-polyoxyethylene (2.0)-2,2-bis(4-hydroxyphenyl)propane, Polyoxypropylene (6)-2,2-bis(4-hydroxyphenyl)propane, Polyoxypropylene (2.2)-2,2-bis(4-hydroxyphenyl)propane, Bisphenol A alkylene oxide adduct **, such as polyoxypropylene (2.4)-2,2-bis(4-hydroxyphenyl)propane and polyoxypropylene (3.3)-2,2-bis(4-hydroxyphenyl)propane, are mentioned. Cyclic aliphatic series diol and the aromatic diol of diol are preferred, and its aromatic diol is more preferred.

[0016]

As polybasic acid of three or more organic functions, trimellitic acid, trimellitic anhydride, pyromellitic acid, pyromellitic dianhydride, etc. are mentioned, for example.

[0017]

As polyhydric alcohol more than trivalent, for example Sorbitol, 1,2,3,6-hexanetetraol, 1,4-sorbitan, pentaerythritol, 1,2,4-butanetriol, 1,2,5-pentanetriol, glycerin, isobutane triol, Aromatic polyhydric alcohol, such as aliphatic-polyhydric-alcohol; 1,3,5-TORIMECHI roll benzene, such as 2-methyl-1,2,4-butanetriol, trimethylolethane, and trimethylolpropane, etc. are mentioned.

[0018]

said dicarboxylic acid carried out, its anhydride, diol, polybasic acid of three or more organic functions, and polyhydric alcohol of three or more organic functions may be used alone, respectively -- it may carry out and two or more sorts may be used together.

[0019]

Since it can distribute stably in supercritical fluid, said polyester resin has preferred polyester resin which has poly dimethylsiloxane structure. Polyester resin which has poly dimethylsiloxane structure has preferred polyester resin whose content of poly dimethylsiloxane structure is 0.1 to 15 % of the weight, and its 1 to 5 % of the weight is more preferred.

[0020]

Polyester resin which has said poly dimethylsiloxane structure can be prepared by the following methods.

1 A method to which polyester resin containing a carboxyl group and poly dimethylsiloxane containing a hydroxyl group are made to react.

2 How to prepare polyester resin as a part of diol used when preparing polyester resin using poly dimethylsiloxane containing two hydroxyl groups which contains two hydroxyl groups in one end preferably.

It is 2 especially. ***** is preferred from being easy to adjust content of poly dimethylsiloxane structure.

[0021]

As poly dimethylsiloxane containing said hydroxyl group, poly dimethylsiloxane containing one hydroxyl group, poly dimethylsiloxane which contains two hydroxyl groups in one end, poly dimethylsiloxane which contains every one a total of two hydroxyl groups at the end, etc. are mentioned, for example. It is [these] available in a commercial item. As poly dimethylsiloxane containing one hydroxyl group, For example, Silaplane FM-0411 by Chisso Corp. (average molecular weight 1,000), Silaplane FM-0421 (average molecular weight 5000), Silaplane FM-0425 (average molecular weight 10,000), etc. are mentioned. As poly dimethylsiloxane which contains two hydroxyl groups in one end, For example, Silaplane FM-DA11 by Chisso Corp. (average molecular weight 1000), Silaplane FM-DA21 (average molecular weight 5,000), Silaplane FM-DA26 (average molecular weight 10,000), etc. are mentioned. As poly dimethylsiloxane which contains every one a total of two hydroxyl groups at the end, For example, Silaplane FM-4411 by Chisso Corp. (average molecular weight 1,000), Silaplane FM-4421 (average molecular weight 5000), Silaplane FM-4425 (average molecular weight 10,000), etc. are mentioned.

[0022]

As for an average molecular weight of poly dimethylsiloxane used for preparation of polyester resin which has poly dimethylsiloxane structure, 500-12000 are preferred, and 3000-11000 are more preferred.

[0023]

Next, a manufacturing method of this invention is explained in detail.

as a method desirable as a manufacturing method of this invention -- for example

(1) A process of manufacturing a resin melting object which carried out melt kneading of the thermoplastics (B) using a pressurized kneader, a three heating roll, a biaxial extrusion kneading machine, etc.,

(2) next -- distributing a resin melting object by a mechanical means by a molten state in supercritical fluid produced by 25 ** and 101.3KPa by carrying out application-of-pressure heating of the compound (A) used as a gas more than the critical pressure of a compound (A), and more than critical temperature -- a thermoplastics grain -- a henchman -- a process of manufacturing a powder object, (3) decompressing with forced cooling of a system promptly preferably, and making a compound (A) evaporate -- a thermoplastics grain -- a henchman -- a process of removing a compound (A) from a powder object,

A manufacturing method which consists of a process to say is mentioned.

[0024]

Supercritical fluid as used in this invention means a fluid in the state where critical temperature peculiar to a substance and the critical pressure were exceeded. For example, carbon dioxide serves as supercritical fluid on condition of 31.1 °C and 7.38MPa. When distributing a resin melting object by a molten state, a compound (A) should just distribute by a system which can maintain a supercritical fluid state, but it is preferred to distribute melting resin in supercritical fluid by a sealing system especially.

Supercritical fluid of supercritical fluid heated more than softening temperature of thermoplastics (B) is preferred, and its supercritical fluid heated at softening temperature - +30 °C of softening temperatures of thermoplastics (B) is more preferred. It is preferred to carry out 300-2000 weight-section use of the supercritical fluid to resin melting object 100 weight section as amount of a resin melting object and supercritical fluid used, and it is more preferred to carry out 500-1500 weight-section use of the supercritical fluid.

[0025]

When distributing a resin melting object in supercritical fluid, For example, what is necessary is to put in and seal a resin melting object in a resisting pressure container which can seal autoclave with agitating equipment, etc., to connect this resisting pressure container and a resisting pressure tank containing supercritical fluid, and just to pour in supercritical fluid into a resisting pressure container under stirring, when distributing by a batch type. When using carbon dioxide for example, as a compound (A) which serves as a gas by said 25 °C and 101.3KPa, supercritical fluid used here, This resisting pressure tank and a liquefied carbonic acid gas bomb accumulated to 5MPa are connected using a resisting pressure tank furnished with a pressure accumulator and a heating machine, What is necessary is to open a valve of a carbon dioxide cylinder, to send carbon dioxide into a pressure accumulator and a heating machine, to change carbon dioxide into a state of supercritical fluid, and just to accumulate into a resisting pressure tank by accumulating pressure and heating. What is necessary is to connect to a dispersion machine of continuous system a resisting pressure tank in which said supercritical fluid is contained using a continuation dispersion machine which can seal and can pressurize a dispersed system, for example, and a tank containing a resin melting object, respectively, and just to distribute by sending them into an agitating equipment portion of a dispersion machine continuously, when continuous system distributes.

[0026]

If a typical commercial item is illustrated as a device to be

used when distributing said continuous system, The Menton gaulin high voltage homogenizer (gaulin company), a continuous system ultrasonic wave homogenizer (NIPPON SEIKI CO., LTD.), There are a nano mizer (nano mizer company), a Micro fluidizer (Mizuho Industries), the Haller type homogenizer, slasher (Mitsui Mining Co., Ltd.), cavitron (incorporated company Euro tech), etc., and cavitron which is a rotary type continuation dispersion device especially is preferred.

[0027]

A stator provided with a projection of ring shape for which said rotary type continuation dispersion device cavitron has a slit, a rotator provided with a projection of ring shape which has a slit maintains an interval -- mutual -- ***** -- it being a rotary type continuation dispersion device which has the structure established on the same axle like, and a dispersion method using this, By making a center section of a stator and a rotator flow in the direction of a periphery from a center section through this slit and this interval, supplying supercritical fluid of a compound (A), and a resin melting object of thermoplastics (B), and rotating a rotator, It is the method of distributing globular form particles of thermoplastics (B) in supercritical fluid of a compound (A).

[0028]

Hereafter, a drawing explains a manufacturing method of this invention using the above rotary type continuous system dispersion devices in detail.

[0029]

A perspective view in which drawing 1 shows an example of a stator of a rotary type continuous system dispersion device used for a manufacturing method of this invention, A perspective view in which drawing 2 shows an example of a rotator of a rotary type continuous system dispersion device used for a manufacturing method of this invention, A sectional view showing an example of an important section of a rotary type continuous system dispersion device which drawing 3 uses for a manufacturing method of this invention, and drawing 4 are the figures showing a combination state of a stator projection when an A-A' section of drawing 3 is seen from the side, and a rotator projection.

[0030]

As shown in drawing 1 - drawing 4, the stator 1 of a rotary type continuation dispersion device was installed in a center, and equips the center with the liquid inlet 2. On a field of a circle configuration of the stator 1, it has the projection 3 put in order by ring shape by stator and a concentric circle in the shape of [one step or two steps or more of] multi stage,

therefore the circumference groove 4 is formed in a gap of projections. And two or more slits 5 are formed among projections.

[0031]

The driving shaft 6 is installed in the center of a wall which counters the stator 1 in this dispersion device, and it is connected to a drive and rotates. The rotator 7 is parallel to the stator 1, and it is being fixed at a tip of a driving shaft so that a center may gather. On a field of the rotator 7 which counters the stator 1, the projection 8 arranged in on a ring by rotator and a concentric circle is equipped in the shape of [one step or two steps or more of] multi stage. Therefore, the annular slot 9 is formed in a gap of projections like a stator. And two or more slits 10 are formed among projections.

[0032]

Use is presented with this stator 1 and rotator 7 in the state where it ***** (ed) so that the projection 3 of the stator 1 and the projection 8 of the rotator 7 may maintain few gaps.

[0033]

When distributing melting resin in supercritical fluid of a compound (A), under sealing, it pressurizes and a dispersed system of this dispersion device is heated so that a supercritical state of a compound (A) can be maintained. And if the rotator 7 rotates a mixture which a resin melting object and supercritical fluid are supplied to the liquid inlet part 2 of this dispersion device, and consists of them, It goes into the slit 10 of the projection 8 of the rotator 7 located in the innermost part, and it is breathed out by the annular slot 9 from the outside of the projection 8 of this rotator 7 according to a centrifugal force, and goes into the slit 5 of the projection 3 of the stator 1 subsequently to the innermost part located. A mixture which flowed into this slit 5 is extruded by the annular slot 4 of the stator 1.

[0034]

Thus, the mixture concerned receives a centrifugal force by rotation of the rotator 7, and flows inside of a slit from a liquid inlet to a delivery. Opening is repeated as a centrifugal flow of a mixture should confine by gap of a slit of the rotator 7 and the stator 1 on the other hand, and differential pressure occurs. Furthermore, shearing force works to mixed liquor in a very small crevice between the rotator 7 and the stator 1. A flow and a circumferential direction flow from this center to an outer peripheral direction collide right-angled, powerful churning and crushing effect occur by it, and a thermoplastic resin particle dispersing element distributed to particle state in supercritical fluid by which a resin melting object was heated by this is obtained. A thermoplastic resin particle

dispersing element is breathed out from a delivery, and are collected on a tank which collects thermoplastic resin particle dispersing elements besides a figure.

[0035]

After a thermoplastic resin particle dispersing element is obtained, cooling and decompression of a system are performed. As for cooling, quenching is preferred. quenching -- a 140 ** thermoplastics grain -- a henchman -- a powder object is performed in 10 seconds to use 65 **. What is necessary is just to perform decompression until it turns into atmospheric pressure (101.3KPa). performing cooling of this system, and decompression -- a thermoplastics grain -- a henchman -- powder -- a compound (A) which exists all over the body as supercritical fluid escapes from a supercritical state, and evaporates a compound (A). It is preferred to perform decompression over 30 minutes or more, and it is more preferred to carry out over 60 to 120 minutes. As a result, without, for example, performing a process of separation from aqueous dispersion of a resin particle, and desiccation indicated with said patent documents 1, a compound (A) can be removed from a dispersing element and a thermoplastic resin particle can be obtained.

[0036]

It is good also as a resin melting object which added paints to thermoplastics (B) and was colored it in a manufacturing method of this invention. As paints used here, for example Hansa yellow 10G, Hansa yellow G. The benzidine yellow G, the benzidine yellow GR, a permanent orange, Resole first orange 3GR, the permanent orange G TR, Balkan fast orange G G, Permanent Red 4R, fire red, p-Krol o-nitroaniline red, Brilliant Fast Scarlet, Brilliant carmine BS, pyrazolone red, Lithol Red, Lake Red C. Lake Red D, brilliant scarlet G, Permanent Red F5R, Brilliant carmine 6B, pigment scarlet 3B, a rhodamine rake (fanal color), An alizarin rake, a toluidine maroon, permanent Bordeaux F2R, The helio bordeaux BL, Bordeaux 10B, a BOMMA lune light, a BOMMA lune medium, A thioindigo maroon, perylene red, Permanent Red BL, Permanent pink E (FH), copper phthalocyanine blue, Fast Sky Blue, indanthrene blue RS, the pigment green B, the naphthol green B, green gold, Phthalocyanine Green, The Naphthol Yellow S rake, a quinoline yellow rake, a pel cyanogen orange, a peacock blue rake, an acid green rake, Para Red, Bordeaux 5B, the Alkali Blue Toner aniline black, carbon black, etc. are mentioned.

[0037]

When using a thermoplastic resin particle obtained by this invention as magnetic toner, it is good also as a resin

melting object to consider it as a magnetic material and use together a tri-iron tetraoxide, gamma ferric oxide, various ferrite powder, iron powder, etc. with thermoplastics.

[0038]

A thermoplastic resin particle obtained with a manufacturing method of this invention can be especially used preferably as an object for electro photography for toners, although it can use in the field of a toner for electro photography, water color ink, oil based ink, powder coatings, adhesives, etc.

[0039]**

[Example]

An example explains this invention in more detail below. All of the part in an example and % are a weight reference.

[0040]

Example 1

An agitator, a thermometer, a nitrogen gas introducing pipe, and a fractionating column in the flask which it has 576 copies of cyclohexane dimethanol, 1900 copies of 2.2 mol of bisphenol A ethyleneoxide additions, 1494 copies of terephthalic acid, and Silaplane FM-DA21 (the poly dimethylsiloxane which contains two hydroxyl groups in one end by Chisso Corp..) Average molecular weight 5,000 50 copy and four copies of dibutyl tin oxide were taught, heating temperature up was carried out under a nitrogen gas air current and churning, and the dehydrating condensation reaction was performed at 240 **. When acid value became 5 mgKOH/g, the polyester resin which terminates a reaction and has poly dimethylsiloxane structure was prepared. The softening temperature according [the weight average molecular weight of this polyester resin] to 9500 and a ring and ball method was 105 **, and glass transition temperature was 58 **. The content of the poly dimethylsiloxane structure in this polyester resin was 1.2%. This polyester resin is written as polyester resin (1).

[0041]

970 copies of polyester resin (1) and pigment blue 15-3 (blue pigment of phthalocyanine system) 30 copy were heated at 200 ** using 2 rolls, melt kneading of the resin was carried out, and the resin melting object was prepared. This was supplied to the resin melting object tank to which it is attached by cavitron CD1010.

[0042]

The pressure accumulator and the heating machine were attached to the resisting pressure tank attached to cavitron CD1010, and also the cylinder of the liquefied carbon dioxide in which 5MPa is pressurized was connected. The supercritical fluid obtained by opening the valve of a cylinder, sending liquefied carbon dioxide into a pressure

accumulator and a heating machine, performing pressure accumulation and heating, carrying out application-of-pressure heating of the liquefied carbon dioxide at 10MPa and 100 **, and manufacturing the supercritical fluid of carbon dioxide was transported to the resisting pressure tank. The valve of the resisting pressure tank was opened here, the pressure of the dispersed system of cavitron was pressurized at 10MPa, and the temperature of the dispersed system was heated until it became 100 **. When the pressure of the dispersed system was set to 10MPa, the valve of the resisting pressure tank was closed.

[0043]

The resin melting object was sent into cavitron CD1010 at the speed of 100 g/m, having opened the valve of the resin melting object tank and maintaining a molten state. The valve of the resisting pressure tank containing supercritical fluid was opened, and supercritical fluid was sent in at the speed of 1 l./m simultaneously with a resin melting object. The revolving speed of the rotator was 8000 rpm, the resin melting object was distributed in supercritical fluid, and the polyester-resin-particles dispersing element was obtained. The temperature of a dispersing element and the temperature of a dispersed system which shifted to the recovery tank with the critical state of carbon dioxide maintained are 145 **, and cooled these to 65 ** in 10 seconds. The dispersed system was decompressed after that and the pressure of ten dispersed systems was set to 101.3KPa (ordinary pressure). As a result, carbon dioxide was removed from the polyester-resin-particles dispersing element of the recovery tank, and dry polyester resin particles have been collected.

[0044]

After classifying the obtained polyester resin particles with a classifier, the dry blend of 0.2% of R-972 (hydrophobic silica made from Japanese Aerosil) of polyester resin particles and polyester resin particles was carried out, and the spherical blue toner with a mean particle diameter of 6.8 microns was obtained.

[0045]

Five copies of this toner and 95 copies of ferrite carriers (electrical resistance is sentimental 107 ohms) with a mean particle diameter of 80 microns were mixed at the number of rotations of 100 rpm in the 1-l. poly bottle for 1 hour, and the developer was prepared. When electrification quantity was measured by blowing off granular material electrification quantity measuring device TB-200, it was -30microC/g. The clear blue picture in which the picture acquired using this developer and the copying machine for electro photography "U-Bix5000" (Konishi 6 photograph industrial incorporated company) has neither a fogging nor a

blot was acquired. The developing box was filled up with the above-mentioned developer, it drove by the motor, and the compulsive churning examination (endurance simulation test which development does not do) of 200 hours was also done. When electrification quantity was measured 200 hours afterward, it was changeless to electrification quantity at -30microC/g. When the electrical resistance of the carrier after separating a toner in blowing off was measured, it was the same as the 107-ohm centimeter and the electric resistance value before a compulsive churning examination. This toner was a toner with very sufficient endurance which cannot cause carrier contamination easily.

[0046]

Example 2

576 copies of cyclohexane dimethanol, 1900 copies of 2.2 mol of bisphenol A ethyleneoxide additions, 1494 copies of terephthalic acid, and Silaplane FM-DA21 Instead of 50 copies and four copies of dibutyl tin oxide, 192 copies of ethylene glycol, 300 copies of neopentyl glycol, and Silaplane FM-DA26 (the poly dimethylsiloxane which contains two hydroxyl groups in one end by Chisso Corp..) Except having used average molecular weight 5,000 26 copy, 996 copies of terephthalic acid, and 1.0 copy of tetrabutyl titanate, when acid value was set to 9 like Example 1, the polyester resin which terminates a reaction and has poly dimethylsiloxane structure was prepared. The softening temperature according [the weight average molecular weight of this polyester resin] to 10500 and a ring and ball method was 98 **, and glass transition temperature was 56 **. The content of the poly dimethylsiloxane structure in this polyester resin was 1.2%. This polyester resin is written as polyester resin (2).

[0047]

Except having used polyester resin (2) instead of polyester resin (1), the coloring resin melting object was prepared like Example 1, and polyester resin particles were obtained like Example 1 except having replaced the transfer rate of this coloring resin melting object with 150 g/m from 100g/m.

[0048]

After classifying the obtained polyester resin particles with a classifier, the dry blend of 0.2% of R-972 of polyester resin particles and polyester resin particles was carried out, and the spherical blue toner with a mean particle diameter of 7.5 microns was obtained.

[0049]

Five copies of this toner and 95 copies of ferrite carriers (electrical resistance is sentimental 107 ohms) with a mean particle diameter of 80 microns were mixed at the number of rotations of 100 rpm in the 1-l. poly bottle for 1 hour, and

the developer was prepared. When electrification quantity was measured by blowing off granular material electrification quantity measuring device TB-200, it was - 35microC/g. The clear blue picture in which the picture acquired using the copying machine of marketing which uses a selenium photoconductive drum has neither a fogging nor a blot was acquired. The developing box of the commercial copying machine was filled up with the above-mentioned developer, it drove by the motor, and the compulsive churning examination of 200 hours was done. When electrification quantity was measured 200 hours afterward, it was changeless to electrification quantity at - 35microC/g. When the electrical resistance of the carrier after separating a toner in blowing off was measured, it was the same as the 107-ohm centimeter and the electric resistance value before a compulsive churning examination. This toner was a toner with very sufficient endurance which cannot cause carrier contamination easily.

[0050]

[Effect of the Invention]

distributing the melting object of thermoplastics (B) in the manufacturing method of this invention in the supercritical fluid of the compound (A) which serves as a gas by 25 ** and 101.3KPa -- a thermoplastics grain -- a henchman -- a powder object being acquired and, A thermoplastic resin particle can be manufactured without being able to make supercritical fluid evaporate and performing the process of separation or desiccation by escaping from the supercritical state of supercritical fluid.

[Brief Description of the Drawings]

[Drawing 1] It is a perspective view showing an example of the stator of the rotary type continuous system dispersion device used for this invention.

[Drawing 2] It is a perspective view showing an example of the rotator of the rotary type continuous system dispersion device used for this invention.

[Drawing 3] It is a sectional view showing an example of the important section of the rotary type continuous system dispersion device used for this invention.

[Drawing 4] It is a figure showing the combination state of a stator projection when the A-A' part of drawing 3 is seen from the side, and a rotator projection.

[Description of Notations]

- 1 Stator
- 2 Liquid inlet
- 3 The projection of a stator
- 4 The circumference groove of a stator
- 5 The slit of a stator projection
- 6 The driving shaft of a rotator

7 Rotator

8 The projection of a rotator

9 The circumference groove of a rotator

10 The slit of a rotator projection

[Translation done.]